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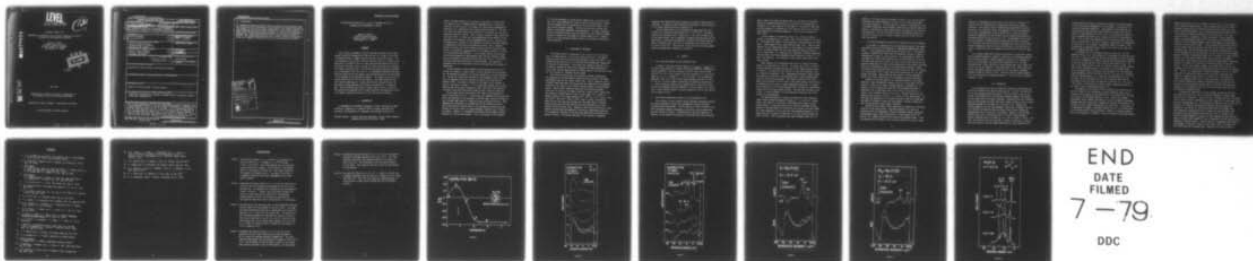
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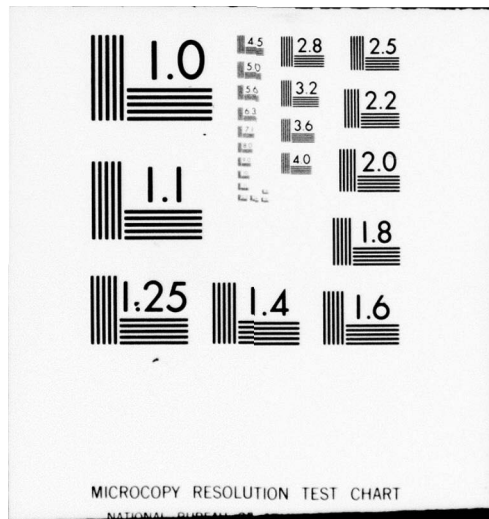
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Technical Report #13

Photoemission Studies of  $H_2S$ ,  $H_2$ , and S Adsorbed on Ru(110):  
Evidence for an Adsorbed SH Species

Galen B. Fisher  
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REF ID: A67112  
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May 1979

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To be published in Surface Science

79 06 15 007

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
9 Technical Report	14 TR-13	
6 TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED	
Photoemission Studies of $H_2S$ , $H_2$ and S Adsorbed on Ru(110): Evidence for an Adsorbed SH Species.		
7. AUTHOR(s)		8. CONTRACT OR GRANT NUMBER(s)
10 Galen B./Fisher		15 N00014-79-F-0014
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Surface Science Division National Bureau of Standards Washington, DC 20234		
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
Office of Naval Research Physical Program Office Arlington, VA 22217		11 May 1979
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		13. NUMBER OF PAGES
12 24p.		
		15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for Public Release; Distribution Unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
Preprint; to be published in Surface Science.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Adsorption, chemisorption, hydrogen, hydrogen-sulfide, ruthenium, surface, ultraviolet photoemission.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)		
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S/N 0102-014-6601

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At intermediate exposures the work function drops and the UPS spectra show new features which are attributed to the presence of an adsorbed SH species. This appears to be the first direct observation of this surface complex. At higher exposures the work function saturates at a value 0.36 eV below the clean value; the UPS spectra change markedly and indicate the adsorption of molecular  $H_2S$ . Heating adsorbed  $H_2S$  leaves a stable layer of S(ads) on Ru(110). The surface with adsorbed sulfur strongly modifies the adsorption at 80 K of a number of molecules relative to the clean Ru(110) surface.

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PHOTOEMISSION STUDIES OF  $\text{H}_2\text{S}$ ,  $\text{H}_2$  AND S ADSORBED ON Ru(110):  
EVIDENCE FOR AN ADSORBED SH SPECIES

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ABSTRACT

$\text{H}_2\text{S}$ ,  $\text{H}_2$  and S adsorbed on Ru(110) have been studied by angle-integrated ultraviolet photoemission (UPS) as part of a study of the effect of adsorbed sulfur, a common catalytic poison, on this Ru surface. For low exposures of  $\text{H}_2\text{S}$  at 80 K, the work function rises to a value 0.16 eV above that of clean Ru(110) while the associated UPS spectra ( $h\nu = 21.2$  eV) exhibit features similar to those of H(ads) and S(ads) and different from those of molecular  $\text{H}_2\text{S}$ . We conclude that  $\text{H}_2\text{S}$  dissociates completely at low coverages on Ru(110) at 80 K. At intermediate exposures the work function drops and the UPS spectra show new features which are attributed to the presence of an adsorbed SH species. This appears to be the first direct observation of this surface complex. At higher exposures the work function saturates at a value 0.36 eV below the clean value; the UPS spectra change markedly and indicate the adsorption of molecular  $\text{H}_2\text{S}$ . Heating adsorbed  $\text{H}_2\text{S}$  leaves a stable layer of S(ads) on Ru(110). The surface with adsorbed sulfur strongly modifies the adsorption at 80 K of a number of molecules relative to the clean Ru(110) surface.

I. INTRODUCTION

A knowledge of the adsorptive behavior of small molecules on metal surfaces is important in a range of fields including catalysis and corrosion. The adsorption of a molecule like hydrogen sulfide is of

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special interest because of its practical importance in these fields. For example,  $\text{H}_2\text{S}$  is a common source of adsorbed sulfur in catalytic reactions for which sulfur is a poison (1), particularly hydrogenation reactions (e.g., methanation and Fischer-Tropsch synthesis). The ease with which  $\text{H}_2\text{S}$  forms stable metal sulfides at interfaces can also be an important materials problem. Since the early studies of  $\text{H}_2\text{S}$  interactions with metal films (2), much work has concentrated on the effects of the adsorbed sulfur produced from  $\text{H}_2\text{S}$  decomposition (1,3,4). Surprisingly few spectroscopic studies of  $\text{H}_2\text{S}$  adsorption on metals have been reported at temperatures below which any desorption occurs (5,6), although a number of optical and electron spectroscopies and work function probes are able to determine in situ whether, for instance, molecular or dissociative adsorption has occurred. In our present effort, we have used ultraviolet photoemission spectroscopy (UPS) and work function change data to characterize the adsorption of  $\text{H}_2\text{S}$  on Ru(110) at  $T \approx 80$  K from fractional monolayer quantities to high coverages. UPS spectra of hydrogen and of sulfur adsorbed on Ru(110) are reported for purposes of comparison.

We have chosen to study hydrogen sulfide adsorption on the (110) surface of ruthenium, a metal which is one of the most active catalysts for the methanation reaction (7) and one susceptible to sulfur poisoning (8). We use the three-digit notation for the hexagonal crystal rather than the redundant four-digit notation in which this face would be denoted  $(11\bar{2}0)$ . The atomic structure of the ideal Ru(110) surface is shown in the inset to Figure 1. It is a more open surface than a close-packed plane and may more successfully mimic the kind of low coordination metal atom sites which may be found on small catalytic particles.

We are aware of only one previous UPS study of  $\text{H}_2\text{S}$  adsorbed on a metal surface near 80 K (5). In that case,  $\text{H}_2\text{S}$  adsorbed on polycrystalline nickel was observed at two coverages to exhibit peaks related to molecular  $\text{H}_2\text{S}$ , although some extent of dissociation was considered possible. When compared with UPS spectra of hydrogen and sulfur adsorbed on Ru(110), the current results indicate that at low coverages  $\text{H}_2\text{S}$  dissociates completely on Ru(110) at 80 K; at high coverages, molecular  $\text{H}_2\text{S}$  is found to be present. However, at intermediate coverages the UPS spectra exhibit features of a new surface species. This is attributed to the presence

of a surface mercaptan or hydro-sulfide complex and is believed to be the first direct observation of such an M-S-H surface species. Hence, the data suggest that  $\text{H}_2\text{S}$  adsorption on Ru(110) at 80 K occurs in at least three successive stages. Initially on the clean surface, the molecule dissociates completely upon adsorption. At higher coverages, partial dissociation occurs and the formation of M-S-H species becomes favorable, possibly as the number of adjacent empty sites is reduced. Finally, as the coverage increases further, only molecular adsorption remains possible.

## II. EXPERIMENTAL PROCEDURE

The single crystal Ru substrate (11 mm x 10 mm x 0.5 mm) was cut with its faces parallel to the (110) plane within  $\pm 1/2^\circ$ . The sample could be cooled to 80 K and resistively heated to more than 1500 K. The temperature was monitored by a 3% Re/W-25% Re/W thermocouple spotwelded to the back of the crystal. The crystal was cleaned by heating in  $\text{O}_2$ , followed by flashing to 1550 K this procedure has been demonstrated using Auger Electron Spectroscopy to produce clean Ru (9) and was verified for this crystal in a separate vacuum system.

The purity of the  $\text{H}_2\text{S}$  gas was verified by the mass spectrometer. The exposures of  $\text{H}_2\text{S}$  were based on measured areas of plots of the mass spectrometer mass 34 ion current versus time. Initial exposures using a rotatable doser were made, but the  $\text{H}_2\text{S}$  was well behaved for the moderate exposures of  $\text{H}_2\text{S}$  used in this liquid-nitrogen-trapped, diffusion-pumped system. Hence, normal exposures were done into the whole chamber. After each run with  $\text{H}_2\text{S}$  the sample contained a stable sulfur layer which was removed by heating several times to about 1500 K for a total of several minutes in an oxygen pressure of  $5 \times 10^{-8}$  to  $1 \times 10^{-7}$  Torr (1 Torr =  $133.3 \text{ N/m}^2 = 133.3 \text{ Pa}$ ). After a final flash in vacuum, the spectrum again had the work function and peak near the Fermi level in the UPS spectra which are both quite sensitive to and characteristic of the surface of Ru(110) being clean. Because of the relative difficulty of the sample cleaning after  $\text{H}_2\text{S}$  exposures, the typical experimental mode was to do sequential exposures of  $\text{H}_2\text{S}$  with data taken before increasing the exposure further. UPS spectra obtained in this fashion for moderate

exposures were reproducible when achieved by different combinations of exposures. No impurity carbon monoxide was detected in the UPS spectra or in thermal desorption after a complete run.

The UHV system used in this experiment has been previously described (10,11) and has a base pressure of  $1 \times 10^{-10}$  Torr. The photoelectrons are excited by He I radiation ( $h\nu = 21.2$  eV) incident at  $45^\circ$  to the sample normal from a windowless microwave discharge lamp and are measured by a three-grid hemispherical retarding field energy analyzer with a collection solid angle of  $0.6\pi$  steradians and a resolution of 0.12 eV at 20 eV (10). The precision of the work function measurements based on photoemission thresholds is  $\pm 0.05$  eV.

### III. RESULTS

#### A. Work Function Changes for $H_2S$ Adsorbed at 80 K

In Figure 1 the work function change ( $\Delta\phi = \phi_{\text{covered}} - \phi_{\text{clean}}$ ) as a function of  $H_2S$  exposure is plotted from the photoelectric thresholds at various exposures. The work function initially rises from the clean value of  $5.0 \pm 0.1$  eV for clean Ru(110) to a maximum of  $\Delta\phi = 0.16$  eV at about 0.9 L (1 L = 1 Langmuir =  $1 \times 10^{-6}$  Torr-sec). For intermediate exposures from 1 to 2 L the surface dipole changes and drops to  $4.64 \pm 0.1$  eV ( $\Delta\phi = -0.36$  eV) where it saturates for exposures of more than 4 L. Since no previous studies of  $H_2S$  adsorption as a function of exposure at low coverages have been reported, it is not known if this variation in work function change is unique or generally true for  $H_2S$  adsorption on metals at 80 K.

#### B. Ultraviolet Photoemission Spectra for $H_2S$ Adsorbed at 80 K

The variation in work function change indicates interesting regions of surface coverage for which the corresponding surface electronic structure should be examined. The UPS spectra in Figure 2 marked a to e with increasing exposure correspond to the hollow circles marked with the same letters in Figure 1. Beginning with the clean spectrum a in Figure 2, we can observe the emission from the Ru(4d,5s) band extending

down to about 6 eV below the Fermi level,  $E_F$ , and then a rising background of scattered electrons which is cut off by the photoelectric threshold (i.e., work function of the sample). The value of the clean surface threshold is indicated by a thin vertical solid line to facilitate comparison at different exposures. A thin line also marks the Fermi level.

As the exposures increase from curve b to d the most dramatic change is the appearance of a strong, broad feature between 5-6 eV below  $E_F$ . The d-band also appears to be selectively attenuated near the Fermi level. There appears to be a weak structure near 12 eV. Each of these features can be related more clearly in the lowest set of spectra where curve c has been redrawn over the clean spectrum along with curve e. Curve e taken after a 3 L exposure has a completely different appearance from the others with three adsorbate-induced features at about 4.1, 7.0, and 9.1 eV below  $E_F$ . Its threshold is also clearly below that of the clean surface.

These spectra can be understood more fully by taking difference spectra, as those shown in Figure 3. The upper curve (e-d) is the difference between the highest and the next to the highest exposure shown in Figure 2. For each the work function is near its saturation value as a function of exposure. This three-peaked difference spectrum shows the electronic structure of the adsorbate that is being adsorbed when the work function has saturated. The relative spacing of the three peaks line up within 0.1 eV of those in the three highest filled orbitals of gaseous  $H_2S$  (12), which is shown immediately above with its vacuum level shifted by 1.6 eV from the photoelectric threshold or experimental vacuum level of the  $H_2S$  covered surface. The fact that the peaks align so well is strong evidence for the existence of molecular  $H_2S$  on the surface at high exposures.

The remaining spectra in Figure 3 are those for lower exposures. These curves represent exposures of about 0.7, 1.4, and 2.0 L, respectively, and they are all plotted as differences with respect to the clean surface. In the lower curve (b-a), the main adsorbate induced feature is centered about 5.8 eV below  $E_F$  and is about 2 eV wide (FWHM). For larger exposures in (c-a) and (d-a) the adsorbate feature at 6 eV grows along with a growth in intensity on its high binding energy side from 7 to 9 eV. Also a completely new feature appears about 12.2 eV

below  $E_F$ . This peak, possibly somewhat shifted in (c-a) by the sloping background due to the threshold, is seen in all of the spectra taken with these exposures. This new feature is present in the spectra at the intermediate exposures (and coverages) where the work function drops but before it saturates at a value determined by the molecular  $H_2S$  found at high exposures. The fact that the new emission centered at about 8 eV and the 12 eV peak grow in together suggests they are related to the same new species.

### C. Ultraviolet Photoemission Spectra for Adsorbed Sulfur and Hydrogen

In an effort to understand the low coverage  $H_2S$  spectra, the sample was heated to drive off the hydrogen to temperatures between 800 K and 1000 K. The  $H_2$  desorption peak occurred at about 180 K. This heating produced a stable sulfur layer whose UPS spectrum is shown in Figure 4. Preexposures of about 2 L and of about 4 L of  $H_2S$  apparently leave the same amount of sulfur after heating since the sulfur peak at 5.8 eV has the same height and area relative to the Ru (4d,5s) band despite the  $H_2S$  exposure being twice as large and the attenuation of the d-band indicating about twice the amount of  $H_2S$  on the surface before heating. Stable surfaces of sulfur adsorbate have also been found on Ni(100) (4), Pt(100) (14), and Fe(100) (15); in each case the half monolayer  $c(2 \times 2)$  LEED pattern was found. Recent LEED and UPS studies of sulfur adsorbed on Ru(001) also find a saturation sulfur coverage of one-half monolayer.

Relative to the  $H_2S$  spectra, an interesting aspect of the S(ads) spectrum is that the dominant feature at 5.8 eV is just where the broad feature is found in the lowest coverage spectra of adsorbed  $H_2S$ . In addition, it is interesting to note that the difference spectrum is completely flat in the region near 12 eV, similar to curve (b-a) in Figure 3, but different than (c-a) or (d-a). The work function of the stable sulfur surface is within 0.1 eV of that of the clean surface. We note that the shoulder at 4.7 eV grows relative to the 5.8 eV peak when the sample is rotated to make the light normally incident, enhancing s-over p-polarization in the incident radiation.

The Ru(110) with S(ads) clearly modifies the adsorption of molecules relative to the clean surface. Negligible amounts of  $H_2$  could be adsorbed at 80 K as determined by UPS and subsequent thermal desorption. Formaldehyde ( $H_2CO$ ), which dissociates to a large degree at 80 K on Ru(110) (11), adsorbs molecularly on the sulfur-poisoned surface. Thus, the adsorbed sulfur present on Ru(110) after heating the  $H_2S$  has clearly

taken up or interfered with the site or sites which are important for dissociation, an important step in adsorption and in many chemical reactions. This sites(s) may be affected upon adsorption at low temperatures or at least well below room temperature since the desorption of  $H_2$  from an adsorbed  $H_2S$  layer at about 180 K is below the normal desorption temperature of the two most tightly bound states found for a hydrogen monolayer at 200 K and 270 K (13). A knowledge of this site(s) would be helpful in understanding the mechanisms of sulfur poisoning. It is possible that the variations in photoemission from sulfur bonding orbitals observed by varying the net polarization of the light may be useful in identifying the site symmetry and position of the sulfur atom (17).

As a further comparison we show the spectrum of a saturation coverage of adsorbed hydrogen in Figure 5, along with its difference spectrum from the clean surface. Thermal desorption studies of  $H_2$  adsorbed on Ru(110) are consistent with dissociative adsorption (13). As does adsorbed sulfur, H(ads) exhibits a strong feature near 6 eV at about 5.6 eV and also has no intensity in the region near 12 eV. Both S(ads) and H(ads) have weaker features on either side of 2 eV where a secondary maximum is seen in Figure 3, (b-a). The work function changes monotonically with coverage for adsorbed hydrogen;  $\Delta\phi$  is 0.5 eV for a saturation coverage (11,13).

#### IV. DISCUSSION

For low exposures of  $H_2S$  to the Ru(110) surface the UPS spectra are distinctly different from that of molecular  $H_2S$ . In fact, the similarity of the low coverage spectrum [Figure 3, (b-a)] to that of a sum of the spectra for adsorbed sulfur and adsorbed hydrogen suggests the presence of both atomic sulfur and atomic hydrogen. Adsorbed sulfur has a dominant peak at 5.8 eV below the Fermi level and a weaker feature at 2.6 eV, while adsorbed hydrogen has two peaks at 5.6 eV and 1.6 eV. Because the absolute amounts of sulfur and hydrogen in each case is unknown, the relative intensity of emission from an adsorbed layer of non-interacting hydrogen and sulfur is difficult to estimate. However, a sum of these spectra should give a strong peak near 5.7 eV and a broad secondary feature (centered about 2 eV below  $E_F$  as is seen in Figure 3, (b-a)). The small work function rise for spectrum b, Figure 2 Figure 2(b) is consistent with the work function change associated with both adsorbed sulfur

and considerably less than a saturation coverage of adsorbed hydrogen, if they were acting independently on the surface. The conclusion is that  $\text{H}_2\text{S}$  dissociates completely. The presence of both molecular and dissociated  $\text{H}_2\text{S}$  has previously been reported to explain UPS and XPS spectra of  $\text{H}_2\text{S}$  adsorbed on Ni at 80 K (5). Also adsorption studies of  $\text{H}_2\text{S}$  on tungsten and nickel (2,18) indicate that  $\text{H}_2\text{S}$  is dissociated at 180 K. This is the first demonstration on a transition metal that  $\text{H}_2\text{S}$  may only dissociate in the initial stages of adsorption for temperatures as low as 80 K. For sp metals the behavior appears different, since dissociation is reported to occur readily on silver (2) and lead (19) only at temperatures near 370 K.

In contrast to its low exposure behavior on Ru(110), for high exposures of  $\text{H}_2\text{S}$  ( $>2 \text{ L}$ ) the surface with a saturated work function value of  $4.64 \pm 0.1 \text{ eV}$  ( $\Delta\phi = -0.36 \text{ eV}$ ) exhibits peak molecular orbital energies with such a resemblance to those of the gas phase photoelectron spectrum of  $\text{H}_2\text{S}$  that we conclude this layer contains pure molecular  $\text{H}_2\text{S}$ . The lack of any relative shift of the  $1b_1$  lone-pair orbital further suggests that no major hydrogen bonding is occurring in this adsorbed layer. This also appears true for molecular  $\text{H}_2\text{S}$  adsorbed on Ni (5), molecular  $\text{CH}_3\text{OH}$  adsorbed on Ru(110) (20) and on Ni(111) (21), but it is different from the reported behavior of a heavy  $\text{H}_2\text{O}$  layer adsorbed on Ni (5). In our case, for  $\text{H}_2\text{S}$  adsorbed on Ru(110) the relaxation energy may be calculated within the simplified approach of Brundle (5). The value is 1.6 eV which is consistent with either a weakly chemisorbed molecule or an initial layer of physisorbed material (5).

The question of the nature of the new species which exists on the Ru(110) surface in the intermediate range of exposures remains to be discussed. This requires an assignment which is consistent with the peak at 12 eV and the increased emission at 8 eV. From  $\text{H}_2$ - $\text{D}_2$  exchange experiments, Saleh, Kemball and Roberts (2) found two types of adsorbed hydrogen when  $\text{H}_2\text{S}$  dissociated on tungsten and discuss the presence of SH radicals as one of several explanations for their data. In our case, it is reasonable to suggest a mercaptan complex since it is a halfway point in the dissociation of the  $\text{H}_2\text{S}$  molecule. However, to provide evidence for an M-S-H species is difficult. We are not aware of published orbital

energy calculations for such a species, so we are left to the "finger-print" method of identification. Most analogous would be UPS spectra of mercaptan species (M-S-H) containing transition metal atoms, but none seem to have been measured. The closest analog available appears to be a study done by Cradock and Whiteford (22) of  $\text{RH}_3\text{SH}$  ( $\text{R} = \text{C}, \text{Si}, \text{Ge}$ ) which are similar to methanol in their structure. The gas phase UPS spectra of the compounds seen with 21.2 eV radiation are reproduced in Figure 6 with the assigned symmetry and the main bonding or non-bonding character of each orbital noted. In this discussion the bonding orbitals within the  $\text{RH}_3$  group are ignored since they do not directly affect our arguments here. The interesting result of Cradock and Whiteford's study for our purposes is that in going from C to Ge in this series the binding energy of the main R-S bonding orbital ( $4a'$ ) is always at a lower binding energy (i.e. less tightly bound) than that of the main S-H bonding orbital ( $3a'$ ) which stays at a fairly constant binding energy (ionization potential) of about 14 eV relative to the vacuum level for the whole series. The  $3a'$  (S-H) orbital appears to be stabilized by the ( $p \rightarrow d$ )  $\pi$ -bonding, since Si and Ge have d-character orbitals available for bonding (22). The  $4a' - 3a'$  separation in  $\text{SiH}_3\text{SH}$  and  $\text{GeH}_3\text{SH}$  is 2.7 eV. In these molecules all the sulfur orbitals are not involved in bonding since there is a lone-pair S( $3p$ ) orbital ( $a''$ ) which lies 4.4 eV above the largely S-H bonding orbital ( $3a'$ ) in both molecules. On the basis of this limited information a tentative conclusion can be drawn that the centroid of the R-S bonding orbitals when all electrons are involved in bonding will lie between 2.7 eV and 4.4 eV less tightly bound than the associated S-H bonding orbital.

To extend this comparison to the Ru surface, we show the relative positions of the  $3a'$ ,  $4a'$ , and  $a''$  orbitals of  $\text{GeH}_3\text{SH}$  (or  $\text{SiH}_3\text{SH}$ ) above spectrum (d-a) in Figure 3. The  $3a'$  orbital is aligned with the 12 eV peak. The  $4a'$  and  $a''$  orbitals (connected by a bar) indeed fall in the range of the emission increase near 8 eV. The electronic structure of R-S-H ( $\text{R} = \text{Si}, \text{Ge}$ ) is certainly not identical to other M-S-H species, but the trends are suggestive. On the Ru(110) surface and other metals we already know that the main M-S bonding orbitals lie about 6 eV from the Fermi level. We propose that the increase in emission near 8 eV is related to M-S orbitals altered somewhat by being in an M-S-H complex and that the peak about 4 eV more tightly bound at 12 eV is consistent with the location of an expected S-H bonding orbital. The S-H orbital is presumably stabilized by the presence of the metal d-orbitals which should tend to increase the M-S-H bond angle and introduce more s character into the S-H orbital.

This explanation is plausible, but not unique. Another possible surface species which could give an orbital in this same energy range would be one involving sulfur dimers. UPS spectra of  $\text{H}_2\text{S}_2$  (23) and  $(\text{CH}_3)_2\text{S}_2$  (24) both exhibit an S-S bonding orbital which could fall in the same spectral range as the 12 eV peak seen in Figure 3. However, this would seem to require a significant surface mobility for S-H or S surface species at 80 K. This does not appear to be indicated by an FEM study of  $\text{H}_2\text{S}$  adsorbed on W at low temperatures (18).

From the evidence it seems reasonable to suggest that the  $\text{H}_2\text{S}$  adsorption begins with dissociation, that M-S-H species are formed, and that molecular adsorption occurs at high coverages. A possible sequence of events can be proposed which may clarify the adsorption process. At low coverages dissociative adsorption dominates the adsorption process probably requiring three empty adjacent sites. This has been discussed for high temperatures during the poisoning of catalytic reactions (1). At intermediate coverages, the probability increases of an adsorbed molecule being at a location with only one other empty site and the complete dissociation of  $\text{H}_2\text{S}$  might not be favorable leaving both M-H and M-S-H species on the surface. At a higher coverage, the  $\text{H}_2\text{S}$  adsorbs molecularly, possibly at sites above the top row of surface atoms (see inset, Figure 1), but more probably by physical adsorption on top of the layer of dissociated species. This sequence also implies that the M-H and M-S species present at low coverages have a positive surface dipole and that the M-S-H species then have an oppositely directed dipole which explains the change in slope of the work function change curve. The work function change then saturates at the negative value characteristic of the surface dipole of molecular  $\text{H}_2\text{S}$ . This is consistent with the negative work function change which has been so far observed for physisorbed gases on transition metals (25). This point of view implicitly assumes that at least M-S and M-S-H species are not exceedingly mobile at 80 K. This would be consistent with the previously mentioned FEM study of  $\text{H}_2\text{S}$  adsorbed on W (18).

In conclusion,  $\text{H}_2\text{S}$  is observed to dissociate on the Ru(110) surface at 80 K. This suggests a small activation energy for this process in this case. The relatively rapid change as a function of exposure from dissociation to partial dissociation to molecular adsorption in this

case reemphasizes the importance of studies using fractional monolayer coverages. More such studies are necessary before the general parameters important in the initial stages of adsorption are understood.

The intermediate coverage UPS spectra and work function change data indicate the presence of a new surface species. Comparisons with gas phase UPS spectra of mercaptan-containing molecules suggest the presence of an M-S-H species on the surface. Other techniques sensitive to surface vibrations should clearly identify such a complex. Further studies with radical species, such as M-S-H or M-O-H, may better define their role in catalytic reactions.

#### ACKNOWLEDGMENTS

The author wishes to thank T. E. Madey and J. T. Yates, Jr. for their encouragement and many helpful discussions throughout the course of this work. D. W. Goodman is gratefully acknowledged for several stimulating and useful discussions. The author acknowledges the Radiation Physics Division of NBS and in particular B. J. Wacławski for the use of the photoemission apparatus described herein. K. Revesz was most helpful in assisting in the data analysis. This work was supported by the Office of Naval Research.

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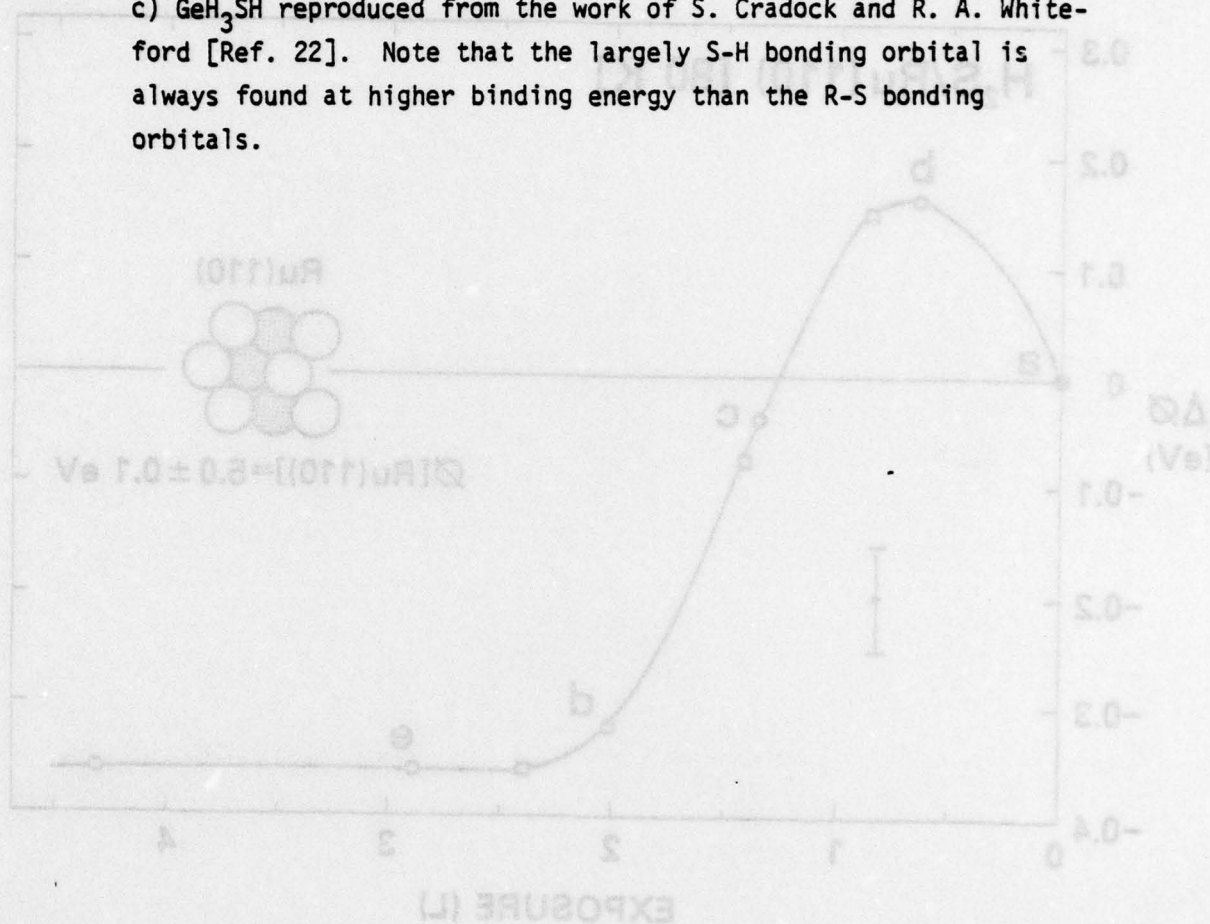
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### FIGURE CAPTIONS

- Figure 1 Work function change,  $\Delta\phi$ , as a function of  $\text{H}_2\text{S}$  exposure on Ru(110) at 80 K (1 L = 1 Langmuir =  $1 \times 10^{-6}$  Torr-sec; 1 Torr =  $133.3 \text{ N/m}^2$ ). Data from separate runs are indicated by hollow circles or squares. The precision of the measurements is indicated by the error bar. The letters correlate with spectra in Figures 2 and 3. The inset at the right is a schematic drawing of the atomic arrangement of the ideal Ru(110) surface.
- Figure 2 Unsmoothed UPS spectra  $[N(E)]$  at  $h\nu = 21.2 \text{ eV}$  for clean Ru(110) [curve a] and for increasing  $\text{H}_2\text{S}$  exposures on Ru(110) at 80 K [curves b-e]. The exposures are indicated by the corresponding letters in Figure 1. Curves c and e have been retraced over curve a to show the relative intensity of the adsorbate-induced features relative to the Ru(4d,5s) band emission. Each spectrum required 8 scans of 256 channels, 0.2 sec/channel.
- Figure 3 UPS spectrum for gas phase  $\text{H}_2\text{S}$  [Ref. 8] and unsmoothed difference spectra  $[\Delta N(E)]$  for  $\text{H}_2\text{S}$  adsorbed on Ru(110) at 80 K. The upper gas phase photoelectron spectrum is referenced to the ionization potential (I.P.) relative to the vacuum level. The spectra are the differences between the indicated  $N(E)$  spectra in Figure 2. The relative positions of the  $3a'$ ,  $4a'$ , and  $a''$  orbitals of gas phase  $\text{GeH}_3\text{SH}$  (Ref. 22) are shown above spectrum (d-a) with the  $3a'$  or largely S-H bonding orbital aligned with the feature at 12 eV in spectrum (d-a).
- Figure 4 Unsmoothed UPS spectrum  $[N(E)]$  at  $h\nu = 21.2 \text{ eV}$  for sulfur adsorbed on Ru(110) after heating an  $\text{H}_2\text{S}$  layer adsorbed at 80 K to above the hydrogen desorption temperature. The clean spectrum taken before the  $\text{H}_2\text{S}$  adsorption is shown as a thin solid line. The difference of the two spectra  $[\Delta N(E)]$  is also shown. Each spectrum required 8 scans of 256 channels, 0.2 sec/channel.

Figure 5 Unsmoothed UPS spectrum  $[N(E)]$  at  $h\nu = 21.2$  eV of a saturation coverage of hydrogen adsorbed on Ru(110) at 80 K. The clean spectrum taken before the hydrogen adsorption is shown as a thin solid line. The difference of the two spectra  $[\Delta N(E)]$  is also shown. Each spectrum required 8 scans of 256 channels, 0.2 sec/channel.

Figure 6 Gas phase UPS spectra at 21.2 eV of: a)  $\text{CH}_3\text{SH}$ , b)  $\text{SiH}_3\text{SH}$ , and c)  $\text{GeH}_3\text{SH}$  reproduced from the work of S. Cradock and R. A. Whiteford [Ref. 22]. Note that the largely S-H bonding orbital is always found at higher binding energy than the R-S bonding orbitals.



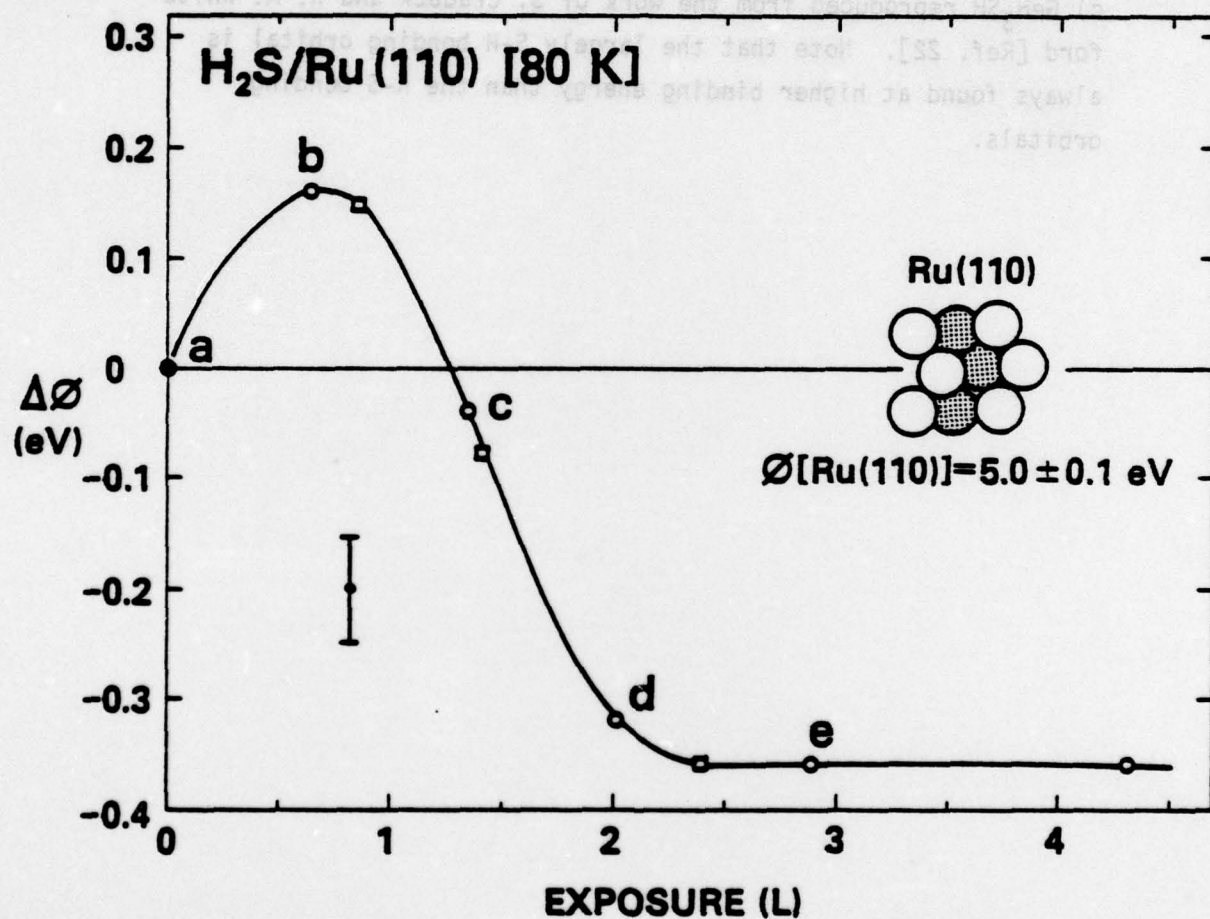


Figure 1

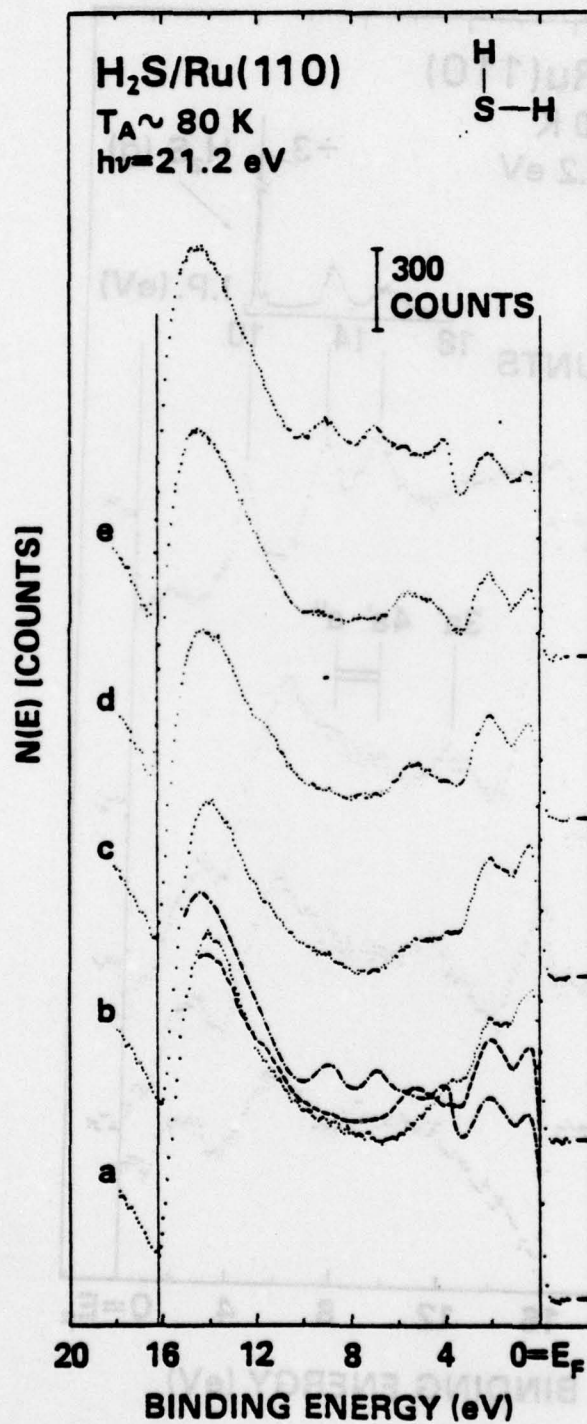


Figure 2

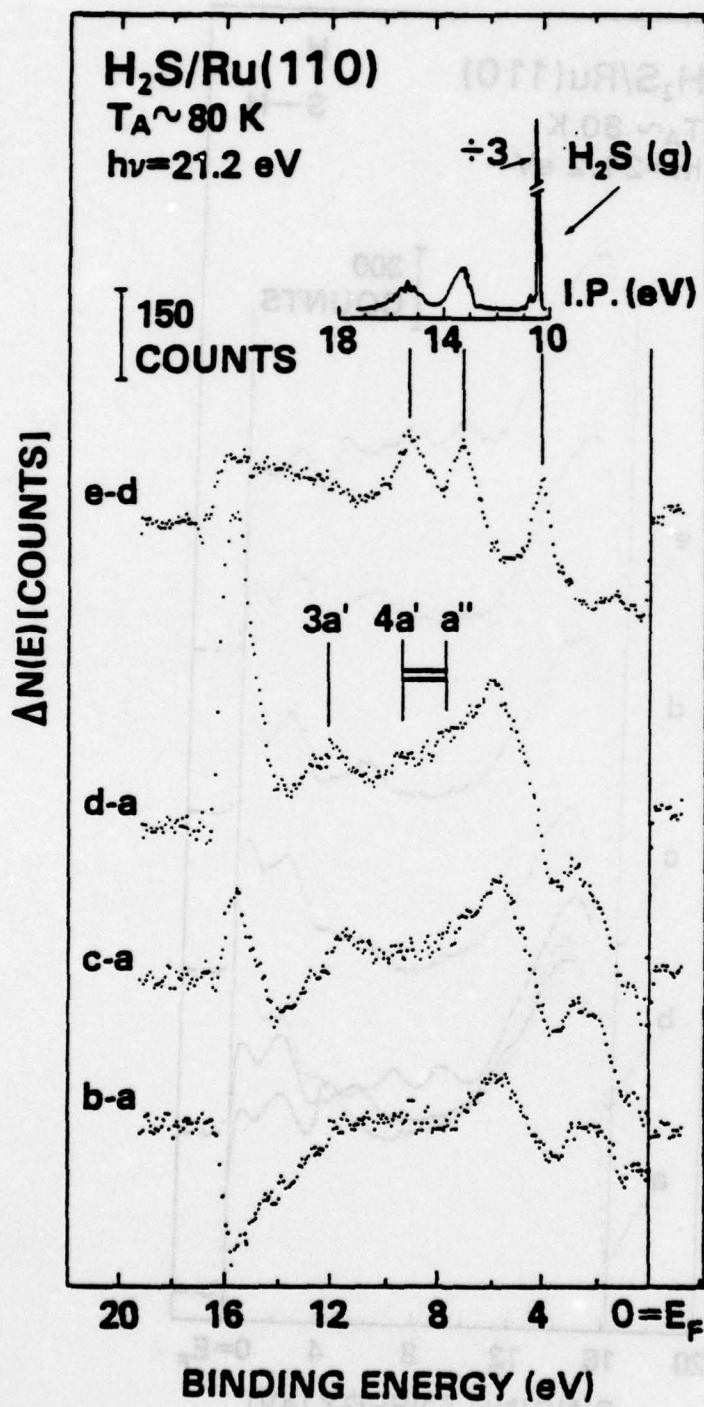


Figure 3

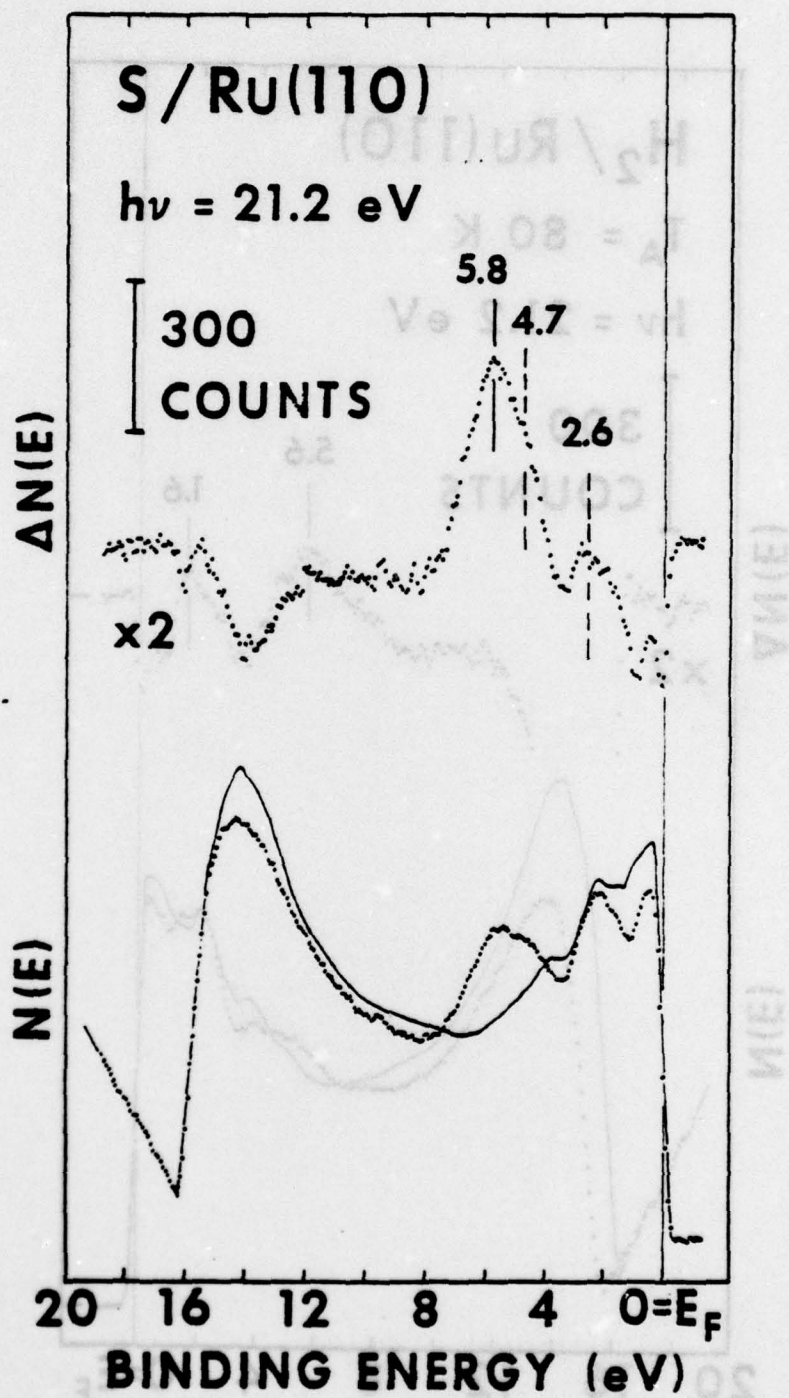


Figure 4

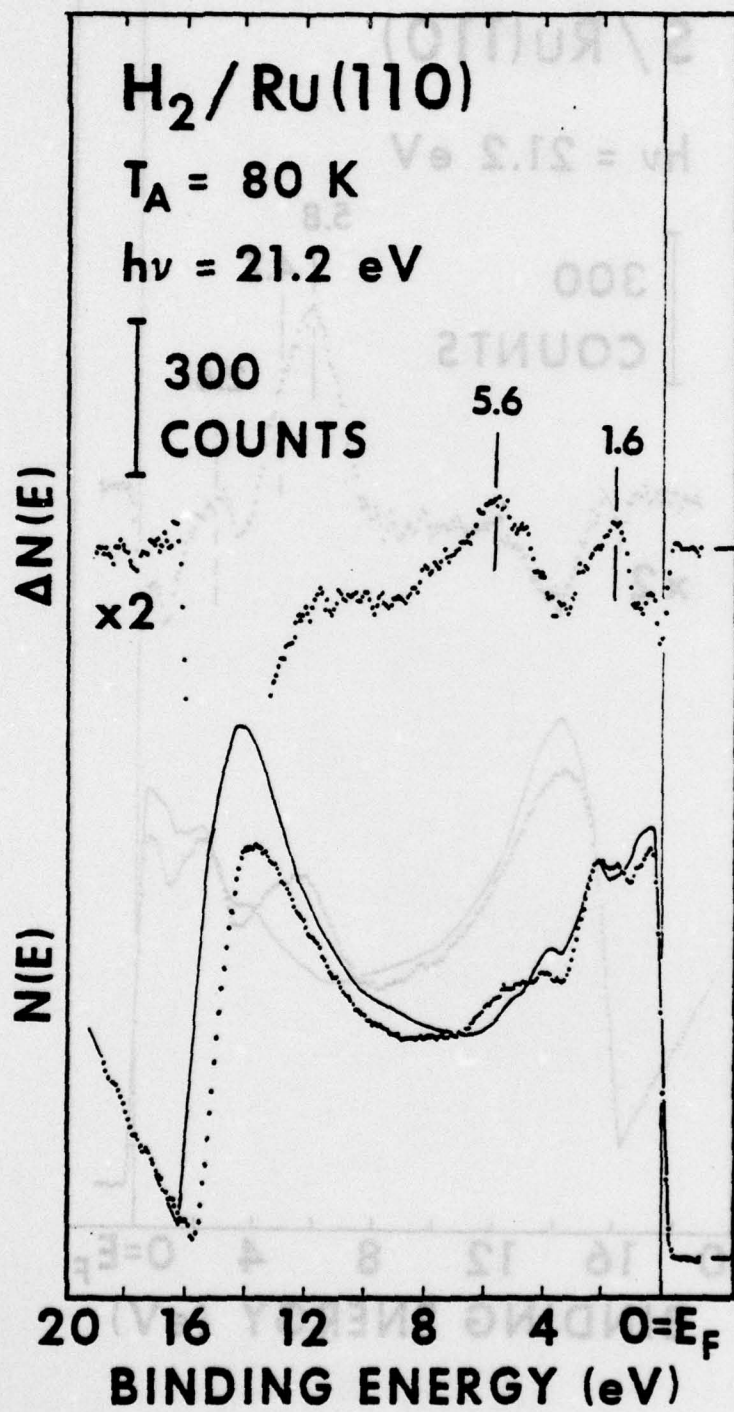


Figure 5

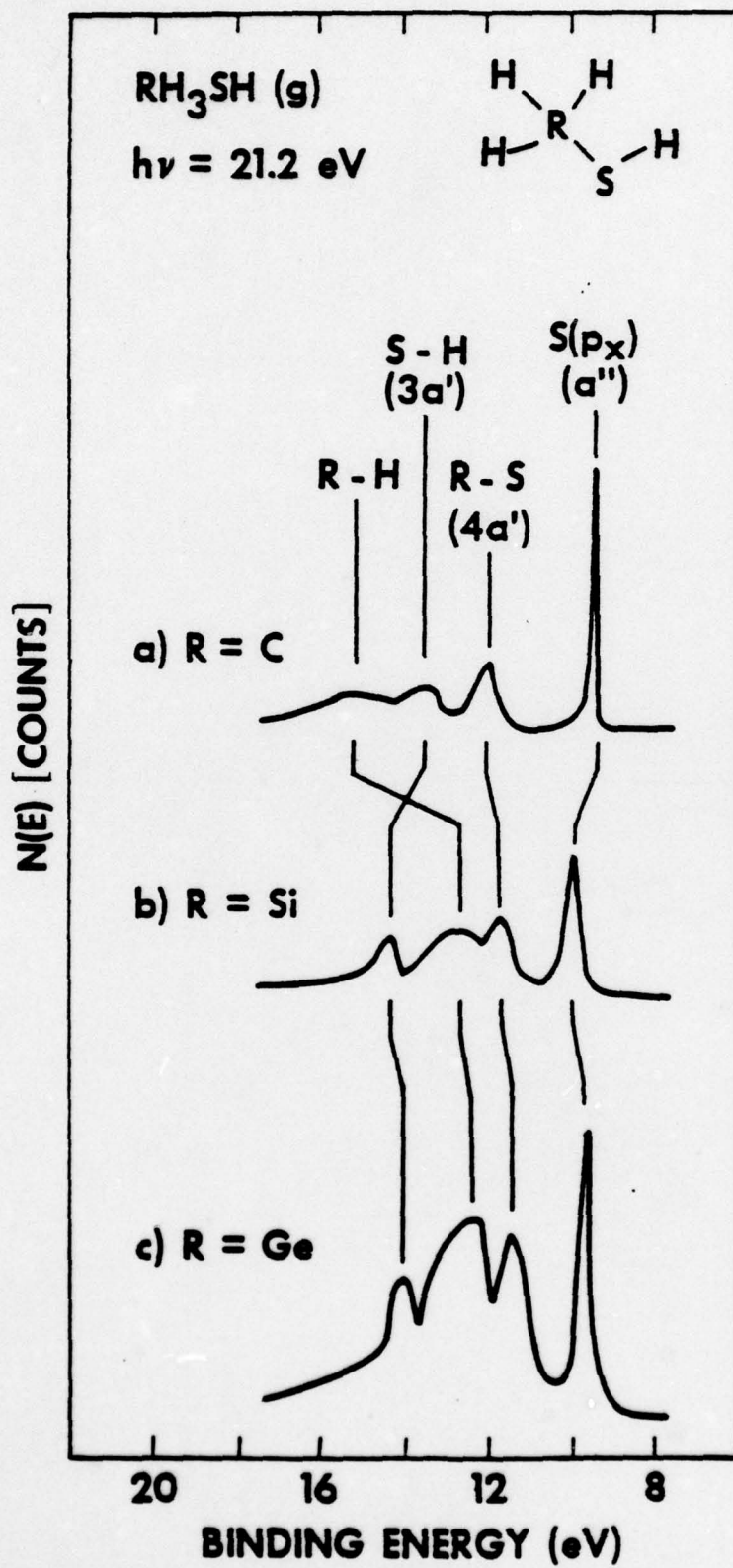


Figure 6